

VII.9 A Metallic Interconnect for Intermediate-Temperature Planar Solid Oxide Fuel Cells (SOFCs)

Tad J. Armstrong (Primary Contact), Anil V. Virkar, Micha Smith, Mike Homel

Materials and Systems Research, Inc.

5395 West 700 South

Salt Lake City, UT 84104

Phone: (801) 530-4987; Fax: (801) 530-4820; E-mail: tarmstro@MSRIhome.com

DOE Project Manager: Lane Wilson

Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- Develop coatings for metallic interconnects for use in intermediate-temperature planar SOFC stacks, with the intent to increase oxidation resistance and electrical conductivity of the interconnect.
- Develop consumptive coatings wherein a metallic coating reacts with the chromium in the alloy to form a stable chromite phase. Examples include Mn and La metal.
- Develop protective coatings, based on spinel and perovskite phases, which are deposited directly onto the alloy substrate and function to decrease the oxidation kinetics of the alloy and suppress the evaporation of chromium species.
- Investigate the oxidation kinetics and electronic properties of coated alloy foils ex-situ (out of stack) and in-situ (in SOFC stack) over a range of temperatures between 600 and 800°C, in air and fuel, over various periods of time.
- Evaluate the performance of internally manifolded SOFC stacks with coated metallic interconnects operated between 600 and 800°C.

Approach

- Identify commercially available alloys, including stainless steels and Ni-Cr super alloys, suitable for use as metallic interconnects in SOFC. Identify spinel and perovskite oxide phases that are potential candidates for coatings, based on the criteria of low ion conductivity but high electronic conductivity.
- Demonstrate consumptive coatings by depositing thin layers of a metal, such as Mn, by physical vapor deposition (PVD) onto a metallic substrate. Upon oxidation, the metal reacts with the chromium in the alloy, promoting the formation of a spinel (or perovskite) phase and suppressing the formation of Cr_2O_3 .
- Fabricate protective coatings wherein a dense layer of a spinel $(\text{Mn,Cr})_3\text{O}_4$ or perovskite $\text{La}(\text{Cr,Mn})\text{O}_3$ phase is deposited onto the alloy by sputtering.
- Measure the oxidation kinetics of coated and uncoated metallic interconnects at temperatures between 600 and 800°C. Develop a model of the oxidation kinetics and fit to the experimentally obtained data.
- Measure the area specific resistance (ASR) of coated and uncoated interconnects as a function of oxidation time and temperature.
- Assemble short stacks of internally manifolded SOFCs with coated interconnects and evaluate the performance under system conditions operating between 600 and 800°C.
- Characterize the crystal chemistry, composition, and assemblage of the phases that form on the alloy interconnects and at the coating interfaces during oxidation.

Accomplishments

- Protective and consumptive coatings have been developed for SOFC metallic interconnects. The coatings suppress formation of Cr_2O_3 , reduce Cr vaporization at high temperature, decrease the oxidation kinetics of the alloy, and increase the electronic conductivity of the oxide layer.
- Protective coatings of the perovskite Sr-doped LaMnO_3 (LSM) and the spinel Mn_2CrO_4 were shown to be effective in reducing the oxidation kinetics. In both cases, the oxidation kinetics exhibited linear behavior with the rate dictated by oxide ion diffusivity in the protective coating.
- The ASR of Cr_2O_3 -forming alloys including Haynes 230 was reduced by over an order of magnitude with the use of consumptive coatings including La, Co, and Mn.
- Coated interconnects were evaluated in internally manifolded, planar SOFC stacks. As compared to uncoated interconnects, the coated interconnects reduced the ASR of the stack by a factor of two, resulting in a doubling of the power density.

Future Directions

- No additional work is planned under this project; however, a large amount of future work and opportunities exist based on the developed methodology.
- Dope the A and B sites of the spinel and perovskite phases to optimize the effectiveness of the coatings with regard to decreasing the ion transport and increasing the electronic conductivity.
- Identify other oxide phases that may be suitable as coating candidates based on their stability in both oxidizing and reducing atmospheres, ionic and electronic conductivity, and thermal expansion coefficient.

Introduction

Chromium-containing alloys are of interest for use as metallic interconnects in planar solid oxide fuel cell stacks due to their good oxidation resistance at temperatures from 600-800°C. However, the Cr-based alloys naturally form a Cr_2O_3 oxide layer which is highly resistive and thus not suitable for interconnect applications. One approach to reducing oxidation kinetics of the alloy and increasing the electronic conductivity of the oxide layer is with the use of coatings. In this work, coating materials were identified and coating methods were developed that significantly improve the oxidation properties of commercially available alloys. Two types of coatings for metallic interconnects were developed: 1) protective coatings and 2) consumptive coatings. The protective coatings were formed by depositing a dense oxide layer directly onto the metallic interconnects. The consumptive coatings were formed by depositing a thin layer of metal onto the interconnect, which upon oxidation would react with the Cr in the alloy to form the desired oxide layer. The chromium-based oxides strongly adhere to the metal, exhibit excellent electronic conductivity, suppress the vaporization of Cr, and serve as a barrier

to oxidation. The coated interconnect samples were oxidized in both fuel and air atmospheres, at different temperatures, and for various periods of time. The oxidation kinetics and electronic conductivity of the coated interconnects were measured and compared to oxidation kinetics models that were developed for both types of coatings. The most promising coated interconnects were tested in planar SOFC stacks.

Approach

Numerous commercially available substrate alloys were investigated in this study, including Haynes 230, Inconels, and various stainless steels. The selection of suitable coating materials was based on the criteria of oxidation resistance and electronic conductivity. Two coating methods were developed: 1) protective coatings and 2) consumptive coatings. The protective coatings were formed by depositing coatings of the desired spinel and perovskite phases directly on the metal substrates by sputtering. Two of the oxides investigated were the perovskite phase $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{3-\delta}$ and the spinel phase Mn_2CrO_4 . Oxide layers with a range of thickness between 0.2 and 2 μm were deposited onto the metallic interconnect foils. The consumptive coatings were

fabricated by depositing thin films of various metals onto the interconnect surface before oxidation. Upon heating, the deposited metal oxidized, reacted with the chromium from the interconnect alloy, and subsequently formed Cr-based oxides other than Cr_2O_3 . For example, a coating of Mn metal on an alloy containing Cr will result in the formation of the more conductive spinel phase $(\text{Mn}, \text{Cr})_3\text{O}_4$, while a coating of La metal will promote the formation of the perovskite phase LaCrO_3 .

In order to study the oxidation kinetics, sample coupons with the consumptive and protective oxide coatings were heated in air and fuel atmospheres (wet and dry) at temperatures between 600 and 800°C for various periods of time and subsequently analyzed with scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), and x-ray diffraction (XRD). Models of the oxidation kinetics of both protective and consumptive coatings were developed and fitted to the experimental data. The electronic conductivity of coated and uncoated samples at various degrees of oxidation was measured in various atmospheres as a function of temperature with a two-probe fixture. Coated and uncoated interconnects were tested in short stacks at temperatures between 600 and 800°C.

Results

Models of the oxidation kinetics of both protective and consumptive coatings were developed for a number of different cases. For the case of the protective coating, the formation of an oxide layer under the protective coating can be modeled in terms of the chemical diffusivity of the participating species. In this case, it is assumed that the oxide ion diffusivity is faster than the cation diffusivity in the coating layer and that the cation diffusivity is faster than the oxide ion diffusivity in the formed oxide layer. For this given scenario, two limiting cases of oxidation kinetics of interconnects with coatings exist: (a) coating limited: with linear growth rate with time, this is the desired case wherein the coating is effective in reducing the oxidation kinetics, and (b) diffusion limited: with parabolic growth rate with time, the coating is ineffective and the growth rate is a function of diffusion in the native oxide. These oxidation kinetics models were validated with experimentally obtained kinetics data.

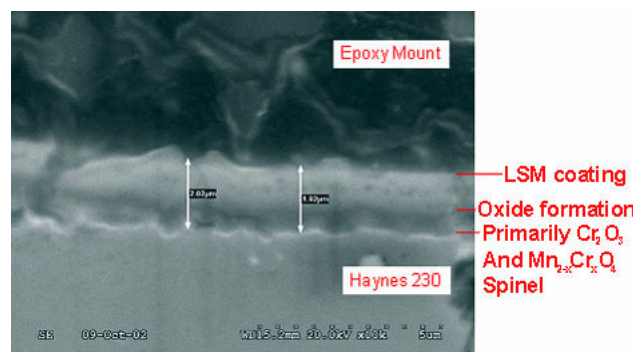


Figure 1. SEM Micrograph Showing a LSM-Coated Haynes 230 Sample after Being Oxidized for 14 Days at 800°C in Air; Secondary Electron Image

The oxidation studies of Haynes 230 samples coated with a dense, protective coating of either LSM or the spinel phase Mn_2CrO_4 were conducted in air at 800°C for various periods of time. Before oxidation, the coatings were $\sim 1.3 \mu\text{m}$ thick and were continuous, dense, and well adhered to the metallic substrate. At various points during the oxidation study, the oxide layers were examined with SEM and characterized for elemental analysis with EDS. A cross-section of a LSM-coated Haynes 230 sample after oxidation for 14 days at 800°C in air is shown in the SEM micrograph in Figure 1. The oxide coating is comprised of two distinct layers: the original deposited LSM coating on the top and a layer of oxide that has formed under the protective LSM coating. The oxide that has formed under the LSM is primarily comprised of Cr_2O_3 and the spinel phase $\text{Mn}_{2-x}\text{Cr}_x\text{O}_4$, which are the native oxides that normally occur on oxidized Haynes 230. The formation of an oxide layer under the protective coating indicates that oxide ions are diffusing through the LSM layer and oxidizing the Cr and Mn contained in the Haynes 230. This is in agreement with one scenario depicted in the proposed kinetics model for a protective coating.

The oxidation kinetics of LSM- and Mn_2CrO_4 -coated Haynes 230 samples were studied at 800°C in air. Initially, a dense layer of oxide coating with a thickness, X_c , of $1.3 \mu\text{m}$ was deposited onto the metal substrates by sputtering. During oxidation, an oxide layer formed under the protective coating with a thickness, X_d . The rate of oxidation is shown in Figure 2 where the total thickness ($X_c + X_d$) is

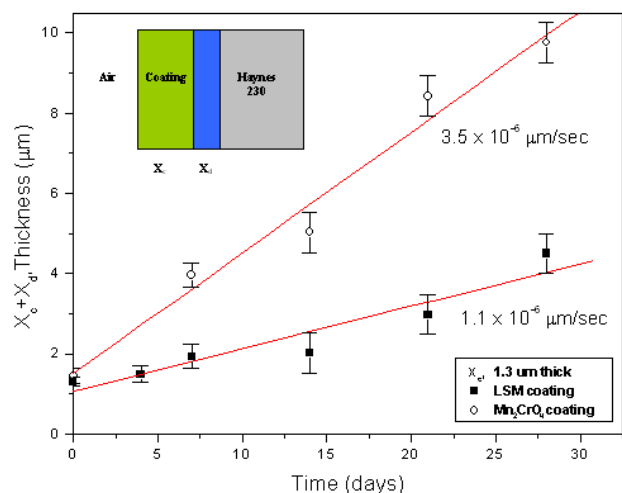


Figure 2. Total Oxide Thickness (X_c and X_d) as a Function of Time for LSM- and Mn_2CrO_4 -Coated Haynes 230 Oxidized at 800°C in Air

plotted as a function of oxidation time for samples with both types of protective oxide coatings. The oxidation rates for samples with both coatings are linear with time, thus indicating a surface rate limiting process. Thus, the oxidation kinetics are dictated and controlled by the protective coating. Based on these growth rates, the chemical diffusivities of the participating species can be estimated by the kinetics model. The chemical diffusivity of oxide ions is $\sim 6 \times 10^{-16} \text{ cm}^2/\text{s}$ in the LSM and $\sim 2 \times 10^{-15} \text{ cm}^2/\text{s}$ in the spinel phase. The thickness of the oxide coating can be predicted for longer times with the model. For an LSM coating of $1.3 \text{ } \mu\text{m}$ and a chemical diffusivity of oxide ions in LSM of $6 \times 10^{-16} \text{ cm}^2/\text{s}$, the oxide thickness as a function of time at 800°C with and without an LSM coating was calculated for the Cr diffusivity of $10^{-13} \text{ cm}^2/\text{s}$, shown in Figure 3. The results show that the coating significantly decreases the oxidation kinetics of the alloys and thus reduces the total thickness of the oxide layer.

Consumptive coatings were developed by depositing thin films of various metals onto the interconnect surface before oxidation. A coating of Mn metal on the Ni-Cr alloys resulted in the formation of the spinel phase $(\text{Mn}, \text{Cr})_3\text{O}_4$, while a coating of La metal resulted in the formation of the perovskite phase LaCrO_3 . Of the materials studied, the spinel formers Mn and Co and the perovskite

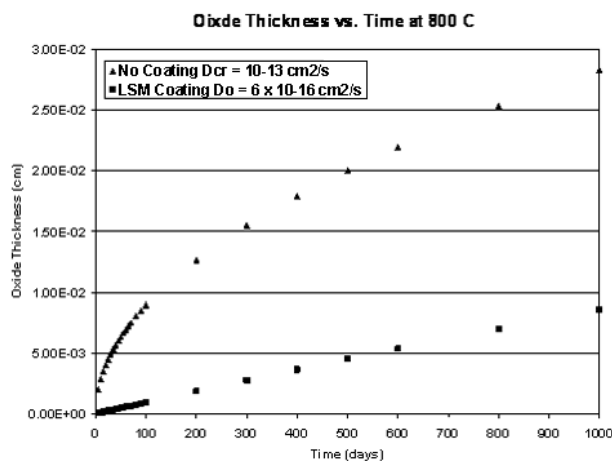


Figure 3. Calculated Oxide Thickness as a Function of Time at 800°C for an Uncoated and LSM-Coated Alloy That Exhibits a Cr Diffusivity of $10^{-13} \text{ cm}^2/\text{s}$

former La were most effective in reducing the ASR of the oxidized interconnect. The Co- and La-coated samples repeatedly and routinely exhibited an ASR one order of magnitude lower than that of the uncoated Haynes 230 samples at 800°C. Coated interconnects were evaluated in short SOFC planar stacks tested at 800°C with air as the oxidant and hydrogen as the fuel. The results of testing 4-cell stacks with this configuration with coated and uncoated interconnects is shown in Figure 4. The

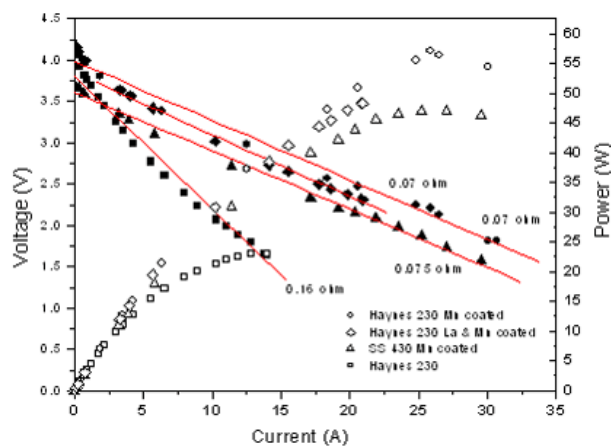


Figure 4. Comparison of the Voltage-Current and Power-Current Characteristics of 4-Cell Planar SOFC Stacks Operating at 800°C with Uncoated Haynes 230, Mn-Coated Haynes 230, Mn-Coated SS 430, and La- & Mn-Coated Haynes 230 Interconnects

ASR of the stacks with the coated Haynes 230 interconnects was one half that of the stacks with the standard uncoated interconnects. Therefore, the coated interconnects reduced the stack resistance and increased the stack power by a factor of two.

Conclusions

Protective and consumptive coatings have been developed for SOFC metallic interconnects. The coatings suppress formation of Cr_2O_3 , reduce Cr vaporization at high temperature, decrease the oxidation kinetics of the alloy, and increase the electronic conductivity of the oxide layer. Oxidation models for both protective and consumptive coatings were developed. Based on the models, two limiting cases of oxidation kinetics of interconnects with coatings exist: (a) coating limited (linear) and (b) diffusion limited (parabolic). Protective coatings of the perovskite LSM and the spinel Mn_2CrO_4 were shown to be effective in reducing the oxidation kinetics. In both cases, the oxidation kinetics

exhibited linear behavior, with the rate dictated by oxide ion diffusivity in the protective coating.

Consumptive coatings that promote the formation of desired oxide phases and suppress the formation of Cr_2O_3 were developed and demonstrated. The ASR of Cr_2O_3 -forming alloys including Haynes 230 was reduced by over an order of magnitude with the use of consumptive coatings including La, Co, and Mn. Coated interconnects were evaluated in internally manifolded, planar SOFC stacks. As compared to uncoated interconnects, the coated interconnects reduced the ASR of the stack by a factor of two, resulting in a doubling of the power density.

FY 2004 Publications/Presentations

1. Poster presented at SECA Core Technology Program Review Meeting, September 30 - October 1, 2003. Albany, New York.